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Notes:

Disolalmer:

- 1. Uniransialable words are replaced with asterisks (****).
- 2. Texts in the figures are not translated and shown as it is.

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Dictionary: Last updated 02/13/2009 / Phority: 1, Chemistry / 2, Natural sciences / 3, Technical term

CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] (A) The group expressed with the repetition unit expressed with a following general formula (I), and -COOR ([R]) When it is the hydrocarbon group which has an alicycle machine, however the carbon atom combined with -COO machine is the 3rd class carbon atom, the hydrocarbon group of the non-acidolysis nature which has an alicycle machine -- expressing -- the positive resist composition containing the compound which generates an acid by the exposure of the resin to which the dissolution rate to alkaline development liquid increases according to the operation of an acid containing the repetition unit which it has and the (B) active light, or radiation.

In a general formula (I), R1 expresses a hydrogen atom or a methyl group, A expresses a single bond or a connecting group, and ALG expresses either a following general formula (pl) - a general formula (pV).

[Formula 2]

$$\begin{array}{c} R_{11} \\ C \\ C \\ C \\ R_{12} \\ C \\ C \\ R_{13} \\ R_{14} \end{array} \qquad (pli)$$

R11 expresses a methyl group, an ethyl group, n-propyl group, an isopropyl group, a n-butyl machine, isobutyl, or sec-butyl among a formula, and Z expresses an atomic group required to form an alicyclic hydrocarbon machine with a carbon atom. R12-R16 express the alkyl group or alicyclic hydrocarbon machine of the normal chain of 1-4 carbon numbers, or branching independently respectively. However, at least one and R15, or R16 express an alicyclic hydrocarbon machine among R12-R14. R17-R21 express the alkyl group or alicyclic hydrocarbon machine of the normal chain of a hydrogen atom and 1-4 carbon numbers, or branching independently respectively, however at least one of R17-R21 expresses an alicyclic hydrocarbon machine. Moreover, R19 or R21 express the alkyl group or alicyclic hydrocarbon machine of the normal chain of 1-4 carbon numbers, or branching. R22-R25 express the alkyl group or alicyclic hydrocarbon machine of the normal chain of 1-4 carbon numbers, or branching independently respectively, however at least one of R22-R25 expresses an alicyclic hydrocarbon machine. Moreover, it may combine with each other and R23 and R24 may form the ring.

[Detailed Description of the Invention] [0001]

[Field of the Invention] This invention relates to positive type photoresist compositions for micro

processing, such as a semiconductor device which induces a far ultraviolet ray, and relates to the positive type photoresist composition for far ultraviolet ray exposure in more detail. [0002]

[Description of the Prior Art] The integrated circuit is raising the degree of location increasingly. and processing of a super-minute pattern which consists of the line width below a half micron in manufacture of semiconductor boards, such as very large scale integration, has come to be needed in recent years. In order to fulfill the necessity, operating wavelength of the photolithography machine used for photo lithography is shortwave-ized increasingly, and by the time using the excimer laser light (XeCl, KrF, ArF, etc.) of short wavelength also in a far ultraviolet ray is now examined, it will become. A chemistry amplification system resist is one of those are used for the pattern formation of the lithography in this wavelength field. [0003] Generally a chemistry amplification system resist can be divided roughly into three kinds, the common-name two-component system, a 2.5 component system, and 3 component system. The two-component system has combined the compound (it is henceforth called the photo-oxide generating agent) and binder resin which generate an acid by a photolysis. This binder resin is resin which has in intramolecular the group (it is also called an acidolysis nature machine) to which an operation of an acid decomposes into and the solubility in the inside of the alkaline development liquid of resin is made to increase. A 2.5 component system contains the low-molecular compound which has an acidolysis nature machine further in such the twocomponent system. 3 component system contains a photo-oxide generating agent, alkalis soluble resin, and the above-mentioned low-molecular compound. [0004] Although the above-mentioned chemistry amplification system resist is suitable for ultraviolet radiation or the photoresist for a far ultraviolet ray exposure, it is necessary to

ultraviolet radiation or the photoresist for a far ultraviolet ray exposure, it is necessary to correspond to the prescribed properties on use further in it. For example, when using the 248nm light of a KrF excimer laser, the resist constituent using the polymer which introduced the acetal group and the ketal machine into the polymer of a hydroxystyrene system especially with little optical absorption as a protective group is proposed. JP,H2-141636,A, JP,H2-19847,A, JP,H4-219757,A, and JP,H5-281745,A each gazette etc. is the example. In addition, the same constituent which uses t-buthoxycarbonyloxy machine and p-tetrahydropyranyloxy machine as an acidolysis machine is proposed by JP,H2-209977,A, JP,H3-206458,A, and JP,H2-19847,A each gazette etc. When using the 248nm light of a KrF excimer laser, even if they are suitable, when using an ArF excimer laser for a light source, since these essentially have too large in addition absorbance, sensitivity is low. There are many points of there being problems, such as the fault of others which furthermore accompany it, for example, deterioration of definition, deterioration of focal tolerance, and deterioration of a pattern profile, and in addition requiring an improvement.

[0005] The resin with which the alicyclic hydrocarbon part was introduced for the purpose of

dry-etching-resistance grant as a photoresist composition for ArF light sources is proposed. The resin which carried out copolymerization of the monomer which has the monomer and hydroxyl group which have a carboxylic acid part called acrylic acid and methacrylic acid as such resin, and a cyano group in intramolecular to the monomer which has an alicyclic hydrocarbon machine is mentioned.

[0006] The method of carrying out dry-etching-resistance grant which utilized the alicyclic hydrocarbon part as a polymer principal chain on the other hand in addition to the method of introducing an alicyclic hydrocarbon part into the side chain of said acrylate system monomer is also examined.

[0007] Moreover, it is in JP,H9-73173,A, JP,H9-90637,A, and JP,H10-161313,A each gazette, The alkali solubility machine protected by structure containing an alicyclic machine and its alkali solubility machine **** with an acid, and the resist material using the acid sensitivity compound including the structural unit made to serve as alkali solubility is indicated. In JP,H11-109632,A, using resin containing a polar group content alicyclic functional group and an acidolysis nature machine for a radiation sensitive material is indicated.

[0008] JP,H7-234511,A has indicated the constituent containing the resin which contains the repetition unit which has an alicycle machine, and the repetition unit which has an acidolysis nature machine as a resist constituent excellent in transparency, ETCHIINGU resistance, high sensitivity, and adhesion. JP,H7-199467,A has indicated the resist constituent containing the copolymer of the acrylate which has the group and carboxylic acid group which cause polar conversion with the repetition unit which has an alicycle machine, and an acid that sensitivity, resolution, and dry ETCHIINGU resistance should be improved (meta).

[0009] As mentioned above, as for resin containing the acidolysis nature machine used for the photoresist for far ultraviolet ray exposure, it is common to intramolecular to contain the cyclic hydrocarbon machine of aliphatic series simultaneously. There are many points still inadequate about the above-mentioned technology, and an improvement is desired. Since various patterns as a tendency of the latest device are contained, the resist is asked for the various performances and it is in one of them that the defocusing latitude of an isolated line pattern is large. An isolated line exists in a device. For this reason, it is important to resolve an isolated line with high reproducibility. However, the present condition is that it is not necessarily easy a thing by an optical factor to make an isolated line reproduce, and the solution by a resist is not clear in. In the resist system which contains the above-mentioned alicycle machine especially, the defocusing latitude of an isolated pattern is narrow and an improvement is desired.

[0010]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the positive type photoresist composition which had the technical problem of the performance improvement technology of above-mentioned micro photofabrication original which uses far ultraviolet light, especially ArF excimer laser light solved. Specifically, it is in offering the outstanding positive type photoresist composition for far ultraviolet ray exposure with a large defocusing latitude of an isolated line pattern.

[0011]

[Means for Solving the Problem] As a result of examining wholeheartedly the component of a positive type chemistry amplification system resist constituent, by the following composition, this invention person etc. found out that the purpose of this invention was attained, and resulted in this invention.

[0012] (1) It is -COOR ([R]) to the repetition unit (A1) and side chain which are expressed with the (A) following general formula (I). When it is the hydrocarbon group which has an alicycle machine, however the carbon atom combined with -COO machine is the 3rd class carbon atom, the hydrocarbon group of the non-acidolysis nature which has an alicycle machine -- expressing -- the positive resist composition containing the compound which generates an acid by the exposure of the resin to which the dissolution rate to alkaline development liquid increases according to the operation of an acid containing the repetition unit (A2) which it has and the (B) active light, or radiation.

[0013]

[Formula 3]

[0014] In a general formula (I), R1 expresses a hydrogen atom or a methyl group, A expresses a single bond or a connecting group, and ALG expresses either a following general formula (pI) - a general formula (pV).

[0015]

[Formula 4]

[0016] R11 expresses a methyl group, an ethyl group, n-propyl group, an isopropyl group, a n-butyl machine, isobutyl, or sec-butyl among a formula, and Z expresses an atomic group required to form an alicyclic hydrocarbon machine with a carbon atom. R12-R16 express the alkyl group or alicyclic hydrocarbon machine of the normal chain of 1-4 carbon numbers, or branching independently respectively. However, at least one and R15, or R16 express an alicyclic hydrocarbon machine among R12-R14. R17-R21 express the alkyl group or alicyclic hydrocarbon machine of the normal chain of a hydrogen atom and 1-4 carbon numbers, or branching independently respectively, however at least one of R17-R21 expresses an alicyclic hydrocarbon machine. Moreover, R19 or R21 express the alkyl group or alicyclic hydrocarbon machine of the normal chain of 1-4 carbon numbers, or branching independently respectively, however at least one of R22-R25 express the alkyl group or alicyclic hydrocarbon machine of the normal chain of 1-4 carbon numbers, or branching independently respectively, however at least one of R22-R25 expresses an alicyclic hydrocarbon machine. Moreover, it may combine with each other and R23 and R24 may form the ring.

[0017] Furthermore, the following composition can be mentioned as a desirable mode. (2) A constituent given in the above (1) characterized by the above-mentioned resin (A) containing the repetition unit further expressed with a following general formula (III). [0018]

[Formula 5]

$$-\left(CH_{2}-C\right) - \left(CH_{2}-C$$

[0019] In a general formula (III), R3 expresses a hydrogen atom or a methyl group. A3 expresses a single bond or a divalent connecting group. Z3 expresses a p+ univalent alicyclic hydrocarbon machine. p expresses the integer of 1-3.

[0020] (3) A positive resist composition given in the above (2) characterized by the repetition unit expressed with a general formula (III) being a repetition unit expressed with a following general formula (IIIa).

[0021]

[Formula 6

[0022] R30 expresses a hydrogen atom or a methyl group among a general formula (IIIa). R31-R33 express a hydrogen atom, a hydroxyl group, or an alkyl group independently respectively, however at least one expresses a hydroxyl group.

[0023] (4) A positive resist composition given in the above (3) characterized by two of R31-R33 being a hydroxyl group in the repetition unit expressed with a general formula (IIIa).

(5) A positive resist composition given in aforementioned (1) - (4) characterized by resin (A) containing further the repetition unit which has cyclohexane lactone, norbornane lactone, or adamantane lactone.

[0024] (6) A positive resist composition given in either of above-mentioned (1) - (5) characterized by for A being a single bond and being the group as which ALG is expressed below in a general formula (I).

[0025]

[Formula 7]

[0026] R26 and R27 express the normal chain of 1-4 carbon numbers, or the alkyl group of branching independently respectively.

[0027]

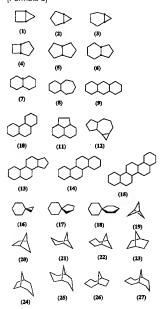
[Embodiment of the Invention] The component used for this invention is explained in detail hereafter

- [1] Resin which the dissolution rate to alkaline development liquid increases according to an operation of the (A) acid (it is also called "acidolysis nature resin").
- [0028] It makes into requirements to contain the acidolysis nature machine content repetition unit (A1) expressed with the above-mentioned general formula (I) as (A) resin in this invention. In a general formula (I), R expresses a hydrogen atom or a methyl group, A expresses a single bond or a connecting group, and ALG is the group containing the alicyclic hydrocarbon shown with the above-mentioned general formula (pI) a general formula (pV).
- [0029] The connecting group of A expresses the combination of independent [which is chosen from the group which consists of an alkylene group, a displacement alkylene group, an ether group, a thioether machine, a carbonyl group, an ester group, an amide group, a sulfonamide machine, a urethane group, or an urea machine], or two groups or more. The group expressed with the following formula can be mentioned as an alkylene group in Above A.
- -The inside of a [C(Rb)] (Rc) r-type, Rb, and Rc A hydrogen atom, an alkyl group, a displacement alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group are expressed, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a displacement alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group (preferably carbon numbers 1-4) can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers of a methoxy group, an ethoxy group, a propoxy group, a butoxy machine, etc. can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. r expresses the integer of 1-10.
- [0030] In general formula (pI) (pV), the normal chain which has 1-4 carbon atoms or the alkyl group of branching which may be displacement or unsubstituted any is expressed as an alkyl group in R12-R25. As the alkyl group, a methyl group, an ethyl group, n-propyl group, an isopropyl group, a n-butyl machine, isobutyl, sec-butyl, t-butyl, etc. are mentioned, for example. Moreover, as further substituent of the above-mentioned alkyl group, the alkoxy group of 1-4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom), an acyl group, an acyloxy machine, a cyano group, a hydroxyl group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. can be mentioned.

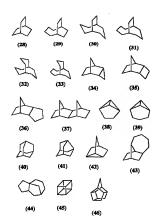
[0031] As an alicyclic hydrocarbon machine which an alicyclic hydrocarbon machine, or Z and

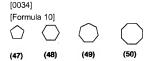
the carbon atom in R11-R25 form, a monocycle type or a polycyclic system is sufficient. Specifically, the group which has with a carbon numbers of five or more mono-cyclo, bicyclo ones, tricyclo one, tetracyclo structure, etc. can be mentioned. As for the carbon number, 6-30 pieces are desirable, and especially its 7-25 carbon numbers are desirable. These alicyclic hydrocarbon machines may have a substituent. Below, the constructional example of an alicyclic portion is shown among alicyclic hydrocarbon machines.

[Formula 8]



[0033] [Formula 9]





[0035] As what has the above-mentioned desirable alicyclic portion in this invention An adamanthyl machine, a NORUADA man chill machine, a decalin residue, a tricyclo deca nil machine, a tetracyclo dodecanyl machine, a norbornyl machine, a cedrol machine, a cyclohexyl machine, a cyclohexyl machine, a cyclo octyl group, a cyclo deca nil machine, and a cyclo dodecanyl machine can be mentioned. They are an adamanthyl machine, a decalin residue, a norbornyl machine, a cedrol machine, a cyclohexyl machine, a cyclohetyl machine, a cyclo octyl group, a cyclo deca nil machine, a cyclo dodecanyl machine, and a tricyclo deca nil machine more preferably.

[0036] As a substituent of these alicyclic hydrocarbon machines, an alkyl group, a displacement alkyl group, a halogen atom, a hydroxyl group, an alkoxy group, a carboxyl group, and an alkoxy carbonyl group are mentioned. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, express the substituent chosen from the group which consists of a methyl group, an ethyl group, a

propyl group, and an isopropyl group desirable still more preferably. As a substituent of a displacement alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As the above-mentioned alkoxy group, the thing of 1-4 carbon numbers of a methoxy group, an ethoxy group, a potoxy group, a butoxy machine, etc. can be mentioned. [0037] In addition, in the general formula (I) from a point (SEM resistance) with little change of the pattern size at the time of observation, A is a single bond in a scanning electron microscope, and especially the repetition unit that is the group as which ALG is expressed below is desirable.

[0038]

[Formula 11]

[0039] R26 and R27 express the normal chain of 1-4 carbon numbers, or the alkyl group of branching independently respectively.

[0040] The example of the monomer which is equivalent to the repetition unit shown with a general formula (I) hereafter is shown.

[0041]

[Formula 12]

2

[0042] [Formula 13] 9 CH₈ CH₉ 0 - CH₉ 10 H O - CH₉ 11 CH₉ CH₉ 0 CH₉ 12 H CH₉ 0 CH₉ 13 CH₉H₉C 0 14 H H₉C 0 16

[0043] [Formula 14]

[0045]

[Formula 16]

[0046]

[Formula 17]

$$= \bigcup_{0}^{CH_3} \bigcup_{0}^{O} \bigcup_{0}^{CH_3} \bigcup_{0}^{CH_3}$$

$$\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{O}
\end{array}$$

[0047] Next, the repetition unit (A2) which has -COOR is explained. R expresses the hydrocarbon group which has the alicycle machine of non-acidolysis nature, when it is the hydrocarbon group which has an alicycle machine, however the carbon atom combined with -COO machine is the 3rd class carbon atom. As an alicycle machine, a monocycle type or a polycyclic system is sufficient here. Specifically, the group which has with a carbon numbers of five or more mono-cyclo, bicyclo one, tricyclo one, tetracyclo structure, etc. can be mentioned. As for the carbon number, 5-30 pieces are desirable, and its 6-15 pieces are [6-25 carbon numbers I especially more desirable still. What was mentioned about the alicyclic hydrocarbon machine which the alicyclic hydrocarbon machine as R11-R25 in the definition of ALG of a general formula (I), or Z and a carbon atom form about the example of an alicycle machine, and the same thing can be mentioned. However, the alicycle machine in R does not have any substituents other than an alkyl group. Although the carbon atom which constitutes alicycle may join together through the oxygen atom and connecting group in -COO-, it is desirable to carry out direct coupling. The alkylene group similarly defined as A in the above-mentioned formula (I) as a connecting group, an ether group, a carbonyl group, ester groups, or such combination can be mentioned. [******] when the carbon atom combined with -COO machine in R is the 3rd class carbon atom and R is the hydrocarbon group which has the alicycle machine of non-acidolysis nature For example, the 3rd class carbon atom of the is a carbon atom which constitutes alicycle, and the case where it has combined with other atoms with which all the three bindings of the 3rd class carbon atom of the constitute alicycle can be mentioned (for example, when the adamanthyl machine is constituted).

[0048] As a repetition unit (A2), the repetition unit expressed with the following general formula (II) can be mentioned, for example.

[0049]

[Formula 18]
$$-\left(CH_{2}-\overset{R_{1}}{C}\right)$$

$$-\left($$

[0050] R1 and A are synonymous with the thing in a formula (I). In addition, the single bond of A is desirable.

[0051] Although the example of a repetition unit (A2) is shown below, it does not limit to these.

[Formula 19]

$$\begin{array}{c} ... \\$$

[0053] As for the above-mentioned resin, it is desirable to contain the repetition unit further expressed with a general formula (III) at the point of improving development nature. [0054]

[Formula 20]

$$-\left(\begin{array}{c} R_{3} \\ I \\ -C \\ A_{3} - Z_{3} - (OH)_{p} \end{array}\right)$$
 (III)

[0055] In a general formula (III), R3 expresses a hydrogen atom or a methyl group. A3 expresses a single bond or a divalent connecting group. Z3 expresses a p+ univalent alicyclic hydrocarbon machine. p expresses the integer of 1-3. That is, -Z3-(OH) p expresses with an

alicyclic hydrocarbon machine the group which p hydroxyl groups replaced.

[0056] The thing same as a divalent connecting group of A3 as A in a general formula (I) can be mentioned, and the same may be said of a desirable group. As an alicyclic hydrocarbon machine of Z3, the alicyclic hydrocarbon machine as R11-R25 in a general formula (I) can be mentioned, and the same may be said of a desirable group. p hydroxyl groups may be replaced by any of the alicyclic hydrocarbon machine of Z3 itself, and the substituent portion which alicyclic hydrocarbon has.

[0057] In addition, the repetition unit expressed with a following general formula (IIIa) is desirable as a repetition unit expressed with a general formula (III) with the point that a large exposure margin is obtained in the case of the line pattern formation by under exposure. [0058]

[Formula 21]

[0059] R30 expresses a hydrogen atom or a methyl group among a general formula (IIIa). R31-R33 express a hydrogen atom, a hydroxyl group, or an alkyl group independently respectively, however at least one expresses a hydroxyl group.

[0060] Moreover, in the repetition unit expressed with a general formula (IIIa) with the point that a large exposure margin is obtained, it is still more desirable in the case of the hole pattern formation by under exposure that two of R31-R33 are a hydroxyl group.

[0061] Although the example of the repetition unit expressed with a general formula (III) below is given, it does not limit to these.

[0062]

[Formula 22]

[0063] [Formula 23]

[0065] Moreover, as for the resin added by the constituent of this invention, it is desirable to contain the repetition unit which has alicycle lactone structure at the point which controls the hole modification at the time of etching. As a repetition unit which has alicycle lactone structure, the repetition unit which has cyclohexane lactone, norbornane lactone, or adamantane lactone can be mentioned, for example.

[0066] for example, as a repetition unit which has cyclohexane lactone The repetition unit which has a following general formula (V-1) and (V-2) the group expressed. The repetition unit which has the group expressed with a following general formula (VI) as the repetition unit which has a following general formula (V-3) and (V-4) the group expressed as a repetition unit which has norbornane lactone, and a repetition unit which has adamantane lactone can be mentioned.

[0067]

[0068] In general formula (V-1) - (V-4), R1 b-R 5b expresses the alkyl group, cycloalkyl machine, or alkenyl group which may have a hydrogen atom and a substituent independently respectively. Two of R1 b-R 5b may form a ring unitedly.

[0069] In general formula (V-1) - (V-4), as an alkyl group in R1 b-R 5b, the shape of a normal chain and a branched state alkyl group are mentioned, and you may have a substituent. As the shape of a normal chain, and a branched state alkyl group, the shape of a normal chain of 1-12 carbon numbers or a branched state alkyl group is desirable. They are the shape of a normal chain of 1-10 carbon numbers, or a branched state alkyl group more preferably. Furthermore, they are a methyl group, an ethyl group, a propyl group, an isopropyl group, a n-

Furthermore, they are a methyl group, an ethyl group, a propyl group, an isopropyl group, a n butyl machine, isobutyl, sec-butyl, t-butyl, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, and a decyl group preferably.

[0070] As a cycloalkyl machine in R1 b-R 5b, the thing of 3-8 carbon numbers, such as a cyclo propyl group, a cyclopentylic group, a cyclohexyl machine, a cycloheptyl machine, and a cyclo octyl group, is desirable. As an alkenyl group in R1 b-R 5b, the thing of 2-6 carbon numbers of a vinyl group, a propenyl machine, a butenyl group, a hexenyl machine, etc. is desirable.

Moreover, as a ring which two of R1 b-R 5b combine and form, three to 8 membered-rings,

such as a cyclopropane ring, a cyclobutane ring, a cyclopentane ring, a cyclohexane ring, and a cyclooctane ring, are mentioned. In addition, R1 b-R 5b in general formula (V-1) - (V-4) may be connected with any of the carbon atom which constitutes the annular frame. [0071] moreover, as a desirable substituent which the above-mentioned alkyl group, a cycloalkyl machine, and an alkenyl group may have The alkoxy group of 1-4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom), the acyl group of carbon numbers 2-5, the acyloxy machine of carbon numbers 2-5, a cyano group, a hydroxyl group, a carboxy group, the alkoxy carbonyl group of carbon numbers 2-5, a nitro group. etc. can be mentioned.

[0072] As a repetition unit which has the group expressed with general formula (V-1) - (V-4), the repetition unit expressed with a following general formula (A.I. Artificial Intelligence) can be mentioned.

[0073]

[0074] Rb0 expresses the displacement or the unsubstituted alkyl group of a hydrogen atom, a halogen atom, or carbon numbers 1-4 among a general formula (A.I. Artificial Intelligence). What was previously illustrated as a desirable substituent which the alkyl group as R1b in said general formula (V-1) - (V-4) may have as a desirable substituent which the alkyl group of Rb0 may have is mentioned. As a halogen atom of Rb0, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. Rb0 has a desirable hydrogen atom. A' expresses a single bond, an ether group, an ester group, a carbonyl group, an alkylene group, or the divalent group that combined these. B-2 expresses the group shown by a general formula (V-1) - (V-4) inner either. In A', the thing of the following type is mentioned as a group of this

[0075]

[Formula 27]

$$\begin{array}{c} -\left(\operatorname{CH_2CH_2} - \operatorname{C}_1 - \operatorname{O} \right)_m \\ -\left(\operatorname{CH_2CH_2} - \operatorname{C}_1 - \operatorname{O} \right)_m \\ -\left(\operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 \right)_m \\ -\left(\operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 \right)_m \\ -\left(\operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 - \operatorname{C}_1 \right)_m \\ -\left(\operatorname{C}_1 - \operatorname{C$$

[0076] In the above-mentioned formula, Rab and Rbb express a hydrogen atom, an alkyl group, a displacement alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a displacement alkyl group, the alkoxy group of a hydroxyl group, a halogen atom, and carbon numbers 1-4 can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers of a methoxy group, an ethoxy group, a propoxy group, a butoxy machine, etc. can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. r1 -- the integer of 1-10 -- the integer of 1-4 is expressed preferably. m -- the integer of 1-3 -- 1 or 2 is expressed preferably.

[0077] Although the example of the repetition unit expressed with a general formula (A.I. Artificial Intelligence) below is given, the contents of this invention are not limited to these.

[0079] [Formula 29]

[0080] [Formula 30]

[0081] [Formula 31]

$$-(CH_{2}-C) \xrightarrow{C} (CH_{2})_{2}-C \xrightarrow{C} (CH_{2})_{2}-C \xrightarrow{C} (CH_{2})_{2}-C \xrightarrow{C} (CH_{3})_{3}$$

[0082] [Formula 32]

[0083] [Formula 33]

[0084] [Formula 34]

$$\begin{array}{c} -(CH_2) \\ -(CH_2) \\$$

[0085] As a repetition unit which has adamantane lactone, the repetition unit expressed with a following general formula (VI) can be mentioned.

[0086]

[Formula 35]

[0087] In a general formula (VI), A6 expresses the combination of independent [which is chosen from the group which consists of a single bond, an alkylene group, a cyclo alkylene group, an ether group, a thioether machine, a carbonyl group, and an ester group], or two

groups or more. R6a expresses a hydrogen atom, the alkyl group of carbon numbers 1-4, a cyano group, or a halogen atom.

[0088] In a general formula (VI), the group expressed with the following type can be mentioned as an alkylene group of A6.

- RnfRng expresses a hydrogen atom, an alkyl group, a displacement alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group among the [C(Rnf)] (Rng) r-above-mentioned type, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a displacement alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of the carbon numbers 1-4 of a methoxy group, an ethoxy group, a propoxy group, a butoxy machine, etc. can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. r is the integer of 1-10.

[0089] In a general formula (VI), as a cyclo alkylene group of A6, ten things are mentioned from a carbon number 3, and a cyclo pentylene machine, a cyclo hexylene machine, ac cyclo octylene machine, etc. can be mentioned.

[0090] The owner pons type alicyclic ring containing Z6 may have a substituent. As a substituent, for example A halogen atom, an alkoxy group (preferably carbon numbers 1-4), An alkoxy carbonyl group (preferably carbon numbers 1-5), an acyl group (For example, a formyl group and benzoyl), an acyloxy machine (for example, propyl carbonyloxy group, a benzoyloxy machine), an alkyl group (preferably carbon numbers 1-4), a carboxyl group, a hydroxyl group, and an alkyl sulfonyl sulfamoyl group (-CONHSO2CH3 grade) are mentioned. In addition, the alkyl group as a substituent may be further replaced by the hydroxyl group, the halogen atom, the alkoxy group (preferably carbon numbers 1-4), etc.

[0091] In a general formula (VI), you may combine the oxygen atom of the ester group combined with A6 in which position of the carbon atom which constitutes the owner pons type alicyclic ring system containing Z6.

[0092] Although the example of the repetition unit expressed with a general formula (VI) below is given, it is not limited to these.

[0093]

[Formula 36]

[0094] [Formula 37]

[0095] Acidolysis nature resin of this invention can contain the repetition unit which has the lactone structure further expressed with a following general formula (IV). [0096]

(Formula 38)

[0097] R1a expresses a hydrogen atom or a methyl group among a general formula (IV). W1 expresses the combination of independent [which is chosen from the group which consists of a single bond, an alkylene group, an ether group, a thioether machine, a carbonyl group, and an ester group], or two groups or more. Ra1, Rb1, Rc1, Rd1, and Re1 express the alkyl group of a hydrogen atom or carbon numbers 1-4 independently respectively. m and n express the integer of 0-3 independently respectively, and m+n is six or less [2 or more].

[0098] As an alkyl group of the carbon numbers 1-4 of Ra1-Re1, a methyl group, an ethyl group, a propyl group, an isopropyl group, a n-butyl machine, isobutyl, sec-butyl, t-butyl, etc. can be mentioned.

[0099] In a general formula (IV), the group expressed with the following type can be mentioned as an alkylene group of W1.

- Rf and Rg express a hydrogen atom, an alkyl group, a displacement alkyl group, a halogen

fluorine atom, iodine atom, etc. can be mentioned.

atom, a hydroxyl group, and an alkoxy group among the [C (Rf) and (Rg)] r1-above-mentioned type, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a displacement alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of the carbon numbers 1-4 of a methoxy group, an ethoxy group, a propoxy group, a butoxy machine. etc. can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom. iodine atom, etc. can be mentioned. r1 is the integer of 1-10. [0100] As further substituent in the above-mentioned alkyl group, a carboxyl group, an acyloxy group, a cyano group, an alkyl group, a displacement alkyl group, a halogen atom, a hydroxyl group, an alkoxy group, a displacement alkoxy group, an acetyl amide group, an alkoxy carbonyl group, and an acyl group are mentioned. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, a cyclo propyl group, cyclo butyl, and a cyclopentylic group, can be mentioned here. As a substituent of a displacement alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. An alkoxy group etc. can be mentioned as a substituent of a displacement alkoxy group. As an alkoxy group, the thing of the carbon numbers 1-4 of a methoxy group, an ethoxy group, a propoxy group, a butoxy machine, etc. can be mentioned. An acetoxy group etc. is mentioned as an acyloxy group. As a halogen atom, a chlorine atom, a bromine atom, a

[0101] Although the example of the monomer which is equivalent to the repetition unit shown with a general formula (IV) hereafter is shown, it is not limited to these.

[0102]

[Formula 39]

[0103] [Formula 40]

[0104] [Formula 41]

[0105] In the example of the above-mentioned general formula (IV), - (IV-36) is desirable from the point that an exposure margin becomes better (IV-17).

[0106] Acidolysis nature resin which is a component in addition to the above-mentioned repetition unit (A) Dry etching resistance and standard developer aptitude, Various repetition units can be contained in order to adjust resolving power, a heat-resisting property, sensitivity, etc. which are substrate adhesion, a resist profile, and the still more general required characteristics of a resist.

[0107] Although the repetition structural unit equivalent to the following monomer can be mentioned as such a repetition unit, it is not limited to these. Performance, solubility [especially as opposed to (1) spreading solvent] which are required of acidolysis nature resin by this, (2) Fine tuning of the adhesion to the substrate of film production nature (glass transition point), (3) alkali development property, (4) film **** (relative-degree-of-intimacy water

and alkali solubility machine selection), and (5) unexposed parts, (6) dry etching resistance, etc. is attained. The compound which has one addition-polymerization nature unsaturated bond chosen, for example from acrylic ester, methacrylic ester, acrylamides, methacrylamide, an allyl compound, vinyl ether, and vinyl ester as such a monomer can be mentioned. [0108] Specifically, the following monomers can be mentioned.

Acrylic ester (the carbon number of an alkyl group is alkyl acrylate of 1-10 preferably): Methyl acrylate, Ethyl acrylate, acrylic acid propyl, acrylic acid amyl, acrylic acid cyclohexyl, Acrylic acid ethylhexyl, acrylic acid octyl, acrylic acid-t-octyl, Chlorethyl acrylate, 2-hydroxyethyl acrylate, 2, and 2-dimethyl hydroxypropyl acrylate, 5-hydroxy pentyl acrylate, trimethylol propane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfurvl acrylate, etc.

[0109] Methacrylic ester (the carbon number of an alkyl group is alkylmetaacrylate of 1-10 preferably): Methyl methacrylate, Ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, Amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, Benzyl methacrylate, benzyl chloride methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl methacrylate, 2, and 2-dimethyl 3-hydroxypropyl methacrylate, trimethylol propane mono-methacrylate, pentaerythritol monomethacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, etc.

[0110] Acrylamides: Acrylamide, N-alkyl acrylamide ([carbon numbers 1-10] as an alkyl group) For example, a methyl group, an ethyl group, a propyl group, butyl, t-butyl, there are a heptyl group, an octyl group, a cyclohexyl machine, a hydroxyethyl machine, etc. N and N-dialkyl acrylamide ([carbon numbers 1-10] as an alkyl group) For example, N-hydroxyethyl N-methyl acrylamide, N-2-acetamidoethyl N-acetyl acrylamide, etc. with a methyl group, an ethyl group, butyl, isobutyl, an ethylhexyl machine, a cyclohexyl machine, etc.

[0111] Methacrylamide: Methacrylamide, N-alkyl methacrylamide ([carbon numbers 1-10] as an alkyl group) For example, a methyl group, an ethyl group, t-butyl, an ethylhexyl machine, a hydroxyethyl machine, N and N-dialkyl methacrylamide (there are an ethyl group, a propyl group, butyl, etc. as an alkyl group) with a cyclohexyl machine etc., N-hydroxyethyl N-methyl methacrylamide, etc.

[0112] Allyl compound: Allyl ester, allyloxy ethanol (for example, an acetic acid allyl compound, allyl caproate, a caprylic acid allyl compound, a lauric acid allyl compound, a palmitic acid allyl compound, a stearic acid allyl compound, allyl benzoate, an acetoacetic acid allyl compound, a lactic acid allyl compound, etc.), etc.

[0113] vinyl ether: — alkyl vinyl ether (for example, hexyl vinyl ether —) Octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, Methoxy ethyl vinyl ether, ethoxyethyl vinyl ether, ethyl chloride vinyl ether, The 1-methyl 2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, Hydroxyethyl vinyl ether, diethylene alvcol vinyl ether, dimethylaminoethyl vinyl ether.

diethylamino ethyl vinyl ether, butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc.

- [0114] Vinyl ester: Vinyl butyrate, vinyl isobutyrate, vinyl bird methyl acetate, Vinyl diethyl acetate, a BINIRUBA rate, vinyl caproate, Vinyl KURORU acetate, vinyl dichloro acetate, vinyl methoxy acetate, vinyl butoxy acetate, vinyl acetoacetate, vinyl lactate, vinyl beta-phenyl butyrate, vinyl cyclohexyl carboxylate, etc. Itaconic acid dialkyls; dimethyl itaconate, itaconic acid diethyl, dibutyl itaconate, etc. The dialkyl ester or monoalkyl ester of boletic acid; dibutylfumarate etc.
- [0115] In addition, crotonic acid, itaconic acid, maleic anhydride, maleimide, acrylonitrile, methacrylonitrile, MAREIRO nitrile, etc.
- [0116] In addition, copolymerization may be carried out as long as it is the monomer which corresponds per [above-mentioned] various repetitions, and the unsaturated compound of copolymerizable addition-polymerization nature.
- [0117] In acidolysis nature resin, the content molar ratio of each repetition unit is suitably set up, in order to adjust resolving power, a heat-resisting property, sensitivity, etc. which are the dry etching resistance of a resist, standard developer aptitude, substrate adhesion, a resist profile, and the still more general necessity performance of a resist.
- [0118] desirable [15 50mol% of the content of the repetition unit (A1) expressed with a general formula (I) / among all the repetition units] among acidolysis nature resin (A) of this invention -- more -- desirable -- 18 46mol % -- they are 20 42mol % still more preferably. desirable [5-30mol% of the content of the repetition unit (A2) which has the group expressed with COOR] among all the repetition units -- more -- desirable -- 8-26mol % -- it is 10-22mol % still more preferably. desirable [5-50mol% of the content of the repetition unit expressed with a general formula (III)] among all the repetition units -- more -- desirable -- 10-45mol % -- it is 15-40mol % still more preferably. desirable [all the 5-60mol% in a repetition unit of the content of a repetition unit which has alicycle lactone structure] -- more -- desirable -- 10-55mol % -- it is 15-50mol % still more preferably. desirable [5 in all the repetition units 60mol% of the content of a repetition unit which has lactone structure in the side chain expressed with a general formula (IV)] -- more -- desirable -- 10 50mol % -- they are 15 45mol % still more preferably. When the constituent of this invention is an object for ArF exposure, as for the point of the transparency to ArF light to acidolysis nature resin, it is desirable not to have an aromatic group.
- [0119] The acidolysis nature resin used for this invention is compoundable according to a conventional method (for example, radical polymerization). For example, as the general synthesis method, are a package or a monomer kind is taught to a reaction container in the middle of a reaction. This if needed A reactional solvent, for example, tetrahydrofuran, 1,4-dioxane. Ether, such as diisopropyl ether, and the ketone like methyl ethyl ketone and methyl

isobutyl ketone Like an ester solvent like ethyl acetate, and the further below-mentioned propylene-glycol-monomethyl-ether acetate After making it dissolve in the solvent in which various monomers may be dissolved and being uniform, a polymerization is made to start using the free-radical initiators (an azo initiator, peroxide, etc.) of heating and marketing if needed under inert gas atmosphere, such as nitrogen and argon. An initiator is added by an addition or fractionation by request, after the end of a reaction, it supplies to a solvent and desired polymer is collected by methods, such as fine particles or solid recovery. The concentration of a reaction is 20 weight % or more, and is 40 weight % or more still more preferably 30weight % or more preferably. Reaction temperature is 10 degrees C - 150 degrees C, and is 50-100 degrees C still more preferably 30 degrees C - 120 degrees C preferably.

[0120] As for the weight average molecular weight of resin concerning this invention, 3,000-100,000 are desirable as a polystyrene reduced property by the GPC method, and they are 5,000-30,000 preferably [it is more desirable and] to 4,000-50,000, and a pan. Since development nature will deteriorate or viscosity will become very high if 100,000 is exceeded preferably [so], since a weight average molecular weight is seen [a heat-resisting property or dry etching resistance deterioration] by less than 3,000, the result which is not so desirable -- film production nature deteriorates -- is produced.

[0121] moreover -- as dispersion (Mw/Mn) of resin concerning this invention, the range of 1.3-4.0 is desirable -- more -- desirable -- 1.4-3.8 -- it is 1.5-3.5 still more preferably.

[0122] In the positive resist composition of this invention, as for the loadings in the whole constituent of all the resin concerning this invention, 40 to 99.99 weight % is desirable among all the resist solid content, and they are 50 to 99.97 weight % more preferably.

[0123] [2] Compound which generates an acid by the exposure of the (B) active light or radiation (photo-oxide generating agent)

The photo-oxide generating agent used by this invention is a compound which generates an acid by the exposure of an active light or radiation.

[0124] As a photo-oxide generating agent used by this invention, the photoinitiator of optical cationic polymerization, a well-known light (400-200nm ultraviolet radiation and a far ultraviolet ray -- [especially] preferably) currently used for the photoinitiator of an optical radical polymerization, the optical decolorizing agent of pigments, optical alterant, or a micro resist The compounds which generate an acid by g line, h line, i line, KrF excimer laser light, ArF excimer laser light, electron rays, X-rays, a molecular beam, or an ion beam, and those mixtures can be used choosing them suitably.

[0125] moreover, as a photo-oxide generating agent used for other this inventions For example, a diazonium salt, ammonium salt, a phosphonium salt, iodonium salt, Onium salt, such as a sulfonium salt, a seleno NIUMU salt, and an arsonium salt. An organic halogenated

compound, an organic metal / organic halide, the photo-oxide generating agent that has onitrobenzyl type protective group, A compound, a disulfon compound, diazo keto sulfone, a diazo disulfon compound, etc. which are represented by imino sulfonate etc. and which carry out a photolysis and generate sulfonic acid can be mentioned. Moreover, the group which generates an acid by such light, or the compound which introduced the compound into the principal chain or side chain of polymer can be used.

[0126] Furthermore, V.N.R.Pillai, Synthesis, (1), 1 (1980), A. Abad etal, Tetrahedron Lett., (47) 4555 (1971), D.H.R. The compound which generates an acid by the light of a description can also be used for Barton etal, J.Chem.Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

[0127] In the compound which decomposes by the exposure of the above-mentioned active light or radiation, and generates an acid, especially other photo-oxide generating agents effectively used together are explained below.

(1) S-triazine derivative expressed with the oxazole derivative or general formula (PAG2) expressed with the following general formula (PAG1) which the trihalomethyl group replaced. [0128]

[Formula 42]

[0129] As for the aryl group which is not replaced [displacement or], an alkenyl group, and R202, R201 shows among a formula the aryl group which is not replaced [displacement or], an alkenyl group, an alkyl group, and -C(Y)3. Y shows a chlorine atom or a bromine atom. Although the following compounds can specifically be mentioned, it is not limited to these. [0130]

[Formula 43]

[0131] (2) The iodonium salt expressed with the following general formula (PAG3), or the sulfonium salt expressed with a general formula (PAG4).

[0132]

[Formula 44]



[0133] Formula Ar1 and Ar2 show respectively the aryl group which is not replaced [displacement or] independently here. R203, R204, and R205 show respectively the alkyl group which is not replaced [displacement or] and an aryl group independently.

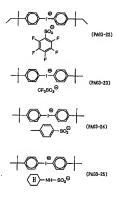
- [0134] Z- is shown and an opposite anion For example, BF4-, AsF6-, PF6-, Perfluoro alkane sulfonic acid anions, such as SbF6-, SiF62-, ClO4-, and CF3SO3-, Condensation polynuclear aromatic series sulfonic acid anions, such as a pentafluoro benzenesulfonic acid anion and a naphthalene 1-sulfonic acid anion, anthraquinone sulfonic acid Although an anion, a sulfonic group content color, etc. can be mentioned, it is not limited to these.
- [0135] Moreover, you may combine two and Ar1 of R203, R204, and R205, and Ar2 through each single bond or substituent.
- [0136] Although the compound shown below as an example is mentioned, it is not limited to these.

[0137]

[Formula 45]

[0138] [Formula 46]

[0139] [Formula 47]



[0140] [Formula 48]

[0141] [Formula 49]

$$(PAG4-18) \\ (PAG4-18) \\ (PAG$$

[0142] [Formula 50]

CF₃SO₃

[Formula 51] PAG4-37

[0144] [Formula 52]

[0146] [Formula 54]

[0147] [Formula 55]

[0148] [Formula 56]

[0149] [Formula 57] CF3(CF2)3SO3-(PAG 4-78)



$$\begin{array}{cccc} & & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

[0151]

CF3(CF2)3SO3-

(PAG 4-91)

[0152] In the above, Ph expresses a phenyl group. a general formula (PAG3) and the above-mentioned onium salt shown by (PAG4) are well-known -- for example, U.S. Pat. No. 2,807,648 -- and -- said -- it is compoundable by the method of a description in No. 4,247,473, a JP,53-101,331.A number, etc.

(PAG4-96)

[0153] (3) The imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with a following general formula (PAG5).

[0154]

[Formula 60]

(PAG4-95)

[0155] Ar3 and Ar4 show respectively the aryl group which is not replaced [displacement or] independently among a formula. R206 shows the alkyl group which is not replaced [displacement or] and an aryl group. A shows the alkylene group which is not replaced [displacement or], an alkenylene group, and an arylene machine.

[0156] Although the compound shown below as an example is mentioned, it is not limited to these.

[0157]

[Formula 61]

[0158] [Formula 62]

(PAG6-19)

(PAGG-20)

[Formula 64]

ormula 64]

$$N = 0 - \frac{1}{8} - CH_3$$
 (PAG6-21)

 $N = 0 - \frac{1}{8} - CF_3$ (PAG6-22)

 $N = 0 - \frac{1}{8} - CH_2$ (PAG6-23)

 $N = 0 - \frac{1}{8} - CH_2$ (PAG6-24)

[0161]

[Formula 65]

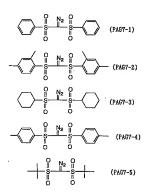
[0162] (4) The diazo disulfon derivative expressed with a following general formula (PAG7). [0163]

[Formula 66]

[0164] R expresses a normal chain, branching, an annular alkyl group, or the aryl group that may be replaced here. Although the compound shown below as an example is mentioned, it is not limited to these.

[0165]

[Formula 67]



[0167] The loadings of these photo-oxide generating agents is usually used in 0.01 to 30weight % of the range on the basis of the solid content in a constituent, and is preferably used in 0.5 to 10weight % of the range still more preferably 0.3 to 20weight %. If there is less loadings of a photo-oxide generating agent than 0.001 weight %, it will become the tendency for sensitivity to become low, and if there is more loadings than 30 weight %, the optical absorption of a resist will become high too much, and there are aggravation of a profile and a tendency for a process (especially bake) margin to become narrow. In addition, in this invention, the compound which decomposes by the exposure of an active light or radiation, and generates sulfonic acid is desirable.

[0168] [3] The positive resist composition of other additive this inventions can be made to contain the compound which promotes the solubility over a surface active agent, an organic base nature compound, an acidolysis nature dissolution inhibition compound, a color, a plasticizer, a photosensitizer, and a developer further if needed.

[0169] (C) the positive resist composition of surface active agent this invention -- a surface active agent -- contain a fluorine system and/or a silicon system surface active agent preferably. As for the positive resist composition of this invention, it is desirable to contain either of the surface active agents containing both a fluorochemical surfactant, a silicon system surface active agent and a fluorine atom, and a silicon atom or two sorts or more. When the positive resist composition of this invention contains the above-mentioned acidolysis nature resin and the above-mentioned surface active agent, especially when the line width of a pattern is much more thin, it is effective, and a developing defect is improved further. As these surface active agents, for example A JP,62-36663, A number, a JP,61-226746, A number, A JP.61-226745.A number, a JP.62-170950.A number, a JP.63-34540.A number, JP.H7-230165,A, JP,H8-62834,A, JP,H9-54432,A, JP,H9-5988,A and U.S. Pat. No. 5405720 number, said 5360692 numbers, said -- No. 5529881 -- said -- No. 5296330 -- said -- No. 5436098 -said -- No. 5576143 -- said -- a surface active agent No. 5294511 and given [this] in No. 5824451 can be mentioned, and the surface active agent of the following marketing can also be used as it is. As a surface active agent of marketing which can be used, for example EFUTOPPUEF301, EF303, (made in new Akita Chemicals), Fluorad FC430, 431 (made by Sumitomo 3M), the mega fuck F171, F173, F176, F189, R08 (made by Dainippon Ink), Fluorochemical surfactants, such as Sir chlorofluocarbon S-382, SC101, 102, 103, 104, 105 and 106 (made by Asahi Glass Co., Ltd.), and Troysol S-366 (made in Troy Chemical), or a silicon system surface active agent can be mentioned. Moreover, polysiloxane polymer KP-341 (made by Shin-Etsu Chemical Co., Ltd.) can be used as a silicon system surface active agent. [0170] The loadings of a surface active agent are usually 0.01 weight % - 1 weight % preferably 0.001 weight % - 2weight % on the basis of the solid content in the constituent of this invention. You may add independently and these surface active agents can also be added in some combination.

[0171] As a surface active agent which can be used besides the above Specifically Polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as polyoxyethylene cetyl ether and polyoxyethylene oleyl ether, Polyoxyethylene alkyl aryl ether, such as polyoxyethylene octyl phenol ether and polyoxyethylene nonyl phenol ether, Polyoxyethylene polyoxypropylene block copolymers Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid ester, such as sorbitan monopalarete, sorbitan trioleate, and sorbitan tristearate, Polyoxyethylene sorbitan monopalarite, polyoxyethylene sorbitan monopalmitate. The Nonion system surface active agents, such as

polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan tristearate, etc. can be mentioned. The loadings of other surface active agents of these of below 2 weight parts are usually below 1 weight part preferably per solid content 100 weight part in the constituent of this invention.

[0172] (D) As for the positive resist composition of organic base nature compound this invention, it is desirable to contain an organic base nature compound. As a desirable organic base nature compound, it is the compound whose basicity is stronger than phenol. A nitrogen-containing basicity compound is especially desirable, for example, the structure expressed with following (A) - (E) is mentioned.

[0173]

[0174] Here [R250, R251, and R252] Respectively, independently, it is the displacement or the unsubstituted aryl group of a hydrogen atom, the alkyl group of carbon numbers 1-6, the amino alkyl group of carbon numbers 1-6, the hydroxyalkyl machine of carbon numbers 1-6, or carbon numbers 6-20, and it may combine with each other and R251 and R252 may form a ring here.

[0175]

[0176] (R253, R254, R255, and R256 show the alkyl group of carbon numbers 1-6 independently respectively among a formula)

Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino group including both ring systems containing the amino group and nitrogen atom which are not replaced [displacement or] preferably. As a desirable example, the aminopyridine which is not replaced [the quanidine which is not

replaced / displacement or / displacement, or], The amino pyrrolidine which is not replaced [the amino alkyl pyridine which is not replaced / displacement or / displacement, or], The pyrazole which is not replaced [in DAZORU which is not replaced / displacement or /, displacement, or], The pyrimidine which is not replaced [the pyrazine which is not replaced / displacement or /, displacement, or], The amino alkyl morpholine which is not replaced [the amino morpholine which is not replaced / the piperazine which is not replaced / the pyrazoline which is not replaced / the pivrazoline which is not replaced / the pivrazoline which is not replaced / the pivrazoline which is not replaced / displacement, or /, displacement, or] is mentioned. Desirable substituents are an amino group, an amino alkyl group, an alkylamino group, an amino aryl group, an arylamino machine, an alkyl group, an alkoxy group, an acyl group, an acyloxy machine, an aryl group, an aryloxy group, a nitro group, an divoxyl group, and a cyano group.

[0177] As a desirable example of a nitrogen-containing basicity compound, guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, 2-aminopyridine, 3-aminopyridine, 4aminopyridine, 2-dimethylamino pyridine, 4-dimethylamino pyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino 3-methylpyridine, 2-amino 4-methylpyridine, 2-amino 5methylpyridine, 2-amino 6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, 3amino pyrrolidine, Piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, The 4amino 2, 2, and 6, 6-tetramethylpiperidine, 4-piperidino piperidine, 2-imino piperidine, 1-(2aminoethyl) pyrrolidine, pyrazole, 3-amino 5-methyl pyrazole, 5-amino 3-methyl 1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, pyrimidine, 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, 1, 5-diazabicyclo [4,3,0] ****- 5-EN, 1, 8-diazabicyclo [5,4,0] undeca 7-EN, 1, 4diazabicyclo [2.2.2] octane. 2.4.5-triphenylimidazole. N-methyl morpholine. N-ethyl morpholine. The 3rd class morpholine derivatives, such as N-hydroxyethyl morpholine, N-benzyl morpholine, and cyclohexyl morpholino ethyl thiourea (CHMETU). Although the hindered amine (for example, thing given in this gazette [0005]) of a description is mentioned to JP,H11-52575.A. it is not limited to this.

[0178] Especially a desirable example 1, 5-diazabicyclo [4.3.0] ****- 5-EN, 1, 8-diazabicyclo [5.4.0] undeca 7-EN, 1, 4-diazabicyclo [2.2.2] octane, 4-dimethylamino pyridine, hexamethylenetetramine, 4, and 4-dimethyl imidazoline, Hindered amine, such as the 3rd class morpholine, such as pyrrole, pyrazole, imidazole derivatives, pyridazines, pyrimidine, and CHMETU, and bis(1, 2, 2, 6, and 6-pentamethyl 4-piperidyl) SEBAGETO, can be mentioned. 1, 5-diazabicyclo [4.3.0] ****- 5-EN, 1, 8-diazabicyclo [5.4.0] undeca 7-EN especially, 1 and 4-diazabicyclo [2.2.2] octane, 4-dimethylamino pyridine, hexamethylenetetramine, CHMETU, and bis(1, 2, 2, 6, and 6-pentamethyl 4-piperidyl) SEBAGETO are desirable. [0179] These nitrogen-containing basicity compounds are independent, or are combined two or

more sorts and used. The amount of the nitrogen-containing basicity compound used is usually 0.01 to 5 weight % preferably 0.001 to 10weight % to the solid content of all the constituents of the resist constituent of this invention. At less than 0.001 weight %, the effect of addition of the above-mentioned nitrogen-containing basicity compound is not acquired. On the other hand, when it exceeds 10 weight %, there is a tendency for the development nature of the fall of sensitivity or a non-exposed area to get worse.

[0180] The positive resist composition of this invention is melted to the solvent which dissolves each above-mentioned component, and is applied on a base material. As a solvent used here, ethylene dichloride, cyclohexanone, Cyclopentanone, 2-heptanone, gamma-butyrolactone, methyl ethyl ketone, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, ethylene glycol monomethyl ether acetate, Propylene glycol monomethyl ether (PGME), propylene-glycol-monomethyl-ether acetate (PGMEA), Ethylene carbonate, toluene, ethyl acetate, butyl acetate, methyl lactate, Ethyl lactate, methoxy methyl propionate, ethoxy ethyl propionate, methyl pruvate, pyruvic acid ethyl, pyruvic acid propyl, N, N dimethylformamide, dimethyl sulfoxide, N-methyl pyrolidone, tetrahydrofuran, etc. are desirable, and independent in these solvents -- or it is mixed and used.

[0181] Also in the above, as a desirable solvent, propylene-glycol-monomethyl-ether acetate, 2-heptanone, gamma-butyrolactone, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, ethylene glycol monoethyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, Ethylene carbonate, bropylene glycol monoethyl ether, Ethylene carbonate, butyl acetate, methyl lactate, ethyl lactate, methoxy methyl propionate, ethoxy ethyl propionate, N-methyl pyrolidone, and tetrahydrofuran can be mentioned.

[0182] Such a positive resist composition of this invention is applied on a substrate, and forms a thin film. As for the thickness of this paint film, 0.2-1.2 micrometers is desirable. As a substrate which can be used, the usual BareSi board, a SOG board, or the substrate that has the inorganic coating of a description next can be mentioned. Moreover, commercial inorganic matter or an organic coating can be used as occasion demands.

[0183] As a coating, inorganic film types, such as titanium, titanium dioxide, titanium nitride, chrome oxide, carbon, and alpha-silicon, and the organic film type which consists of a light absorber and a polymeric material can use. The former needs equipment of a vacuum metallizer, CVD equipment, sputtering equipment, etc. for film formation. As an organic coating, for example The condensation product of a diphenylamine derivative given in a JP,7-69611,B number, and a formaldehyde denaturation melamine resin, What consists of alkalis soluble resin and a light absorber, a maleic anhydride copolymer given in a U.S. Pat. No. 5294680 number, and the reactant of a diamine type light absorber, The thing containing a resin binder given in JP,H6-118631,A, and a methylol melamine system heat cross linking agent. The acrylate resin type coating which has a carboxylic acid group, an epoxy group, and

an extinction machine given in JP,H6-118656,A in the same intramolecular, What consists of methylol melamine and a benzophenone system light absorber given in JP,H8-87115,A, the thing which added the low-molecular light absorber to polyvinyl alcohol resin given in JP,H8-179509,A, etc. are mentioned. Moreover, DUV30 series by BURYUWA Saiensu-Sha, DUV-40 series, ARC25, AC-2 made from SHIPURE, AC-3, AR19, and AR20 grade can also be used as an organic coating.

[0184] If the above-mentioned resist liquid I (on the substrate which was able to prepare the above-mentioned coating as occasion demands) on a substrate (example: silicon / diacid-ized silicon covering) which is used for manufacture of a precision integrated circuit element It can expose through a predetermined mask after spreading by the suitable spreading methods. such as a spinner and coater, and a good resist pattern can be obtained by developing negatives by performing bake. As an exposure light, it is light with a wavelength of 150nm -250nm preferably here. Specifically, a KrF excimer laser (248nm), an ArF excimer laser (193nm), a F2 excimer laser (157nm), X-rays, an electron beam, etc. are mentioned. [0185] As a developer, sodium hydroxide, potassium hydroxide, sodium carbonate, Inorganic alkali, such as sodium silicate, meta-sodium silicate, and aqueous ammonia, Primary amine, such as ethylamine and n-propylamine, diethylamine, Tertiary amine, such as secondary amine, such as G n butylamine, triethylamine, and methyl diethylamine, Alcoholic amines, such as dimethylethanolamine and triethanolamine, Alkaline aqueous solutions, such as annular amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, pyrrole, and PIHERIJIN, can be used. Furthermore, alcohols and a surface active agent can also be used for the above-mentioned alkaline aqueous solution, carrying out adequate amount addition.

[0186]

[Example] Hereafter, although a work example explains this invention still more concretely, this invention is not limited to the following work examples.

[0187] The synthetic 2-adamanthyl 2-propyl methacrylate of synthetic example (1) resin (1), isoboronyl acrylate, norbornane lactone acrylate, and dihydroxy adamantane methacrylate It taught at a rate of 35/15/30/20, and dissolved in PGMEA(propylene-glycol-monomethyl-ether acetate)/PGME(propylene glycol monomethyl ether) = 7 / 3 (bulk density), and 450g of solutions of 22 weight % of solid content concentration were prepared. It is about the Wako Pure Chem make V-601 to this solution. 1mol% -- in addition, this was dropped at PGMEA (propylene-glycol-monomethyl-ether acetate)/PGME(propylene glycol monomethyl ether) = 7 heated at 100 degrees C / 3 (bulk density) or 40g over 6 hours under nitrogen-gas-atmosphere mind. Reaction liquid was agitated after the end of dropping for 4 hours. After cooling reaction liquid to the room temperature after the end of a reaction and separating crystallization and depositing white fine particles to the mixed solvent 5L of water / methanol =1/1, the obtained

fine particles with Methanol 1L, and resin (1) which is an object was collected. [0188] The polymer composition ratio for which it asked from NMR is 2. - It was adamanthyl 2propyl methacrylate / isoboronyl acrylate / norbornane lactone acrylate / dihydroxy adamantane methacrylate =34/14/31/21. Moreover, the weight average molecular weight of the standard polystyrene conversion searched for by GPC measurement was 8600. [0189] By the same operation as the above-mentioned synthetic example, resin (1'), (1"), and (2) - (10) were compounded. Resin (1) The composition of the repetition unit which - (10) has is shown below. Moreover, the ratio of the repetition unit of these resin and a weight average molecular weight are shown in Table 1. The ratio of the repetition unit in Table 1 is the order from the left repetition unit in the composition of the repetition unit shown below. In addition, the composition of resin (1') and (1") the repetition unit which it has is the same as that of resin (1).

[0190]

$$\begin{array}{c} CH_3 \\ -CH_2 - C \\ -CH_$$

[0192]

[Formula 73]

[0193] [Table 1] 表1

樹脂	第1繰り返し単位	第2繰り返し単位	第3繰り返し単位	第4繰り返し単位	分子量
	(A1)	(A2)	(mal%)	(mol96)	
	(mol%)	(mol%)			
1	34	14	31	21	8600
1'	30	10	40	20	9900
1"	30	21	30	19	7900
2	36	16	34	14	8700
3	31	17	28	14	8900
4	29	21	13	37	8300
5	28	19	23	30	9100
6	39	13	24	24	10100
7	41	15	26	18	9700
8	32	16	22	30	7900
9	38	12	30	20	10900
10	27	20	30	23	11600

[0194] The resin [as / in work examples 1-14, a comparative example 1, and two (preparation and evaluation of a positive resist composition constituent) table 2] (2g) compounded in the above-mentioned synthetic example, a photo-oxide generating agent (loadings were shown in Table 2), an organic base nature compound (4mg), and necessity The surface active agent (10mg) was blended, after dissolving in the solvent shown with becoming 14 weight % of solid content in Table 2, it filtered with the 0.1-micrometer micro filter, and the positive resist composition of work examples 1-14 and comparative examples 1 and 2 was prepared. In addition, the ratio in the case of two or more use about each component in Table 2 is a bulk density.

[0195] In addition, the resin R1 used for the comparative example 1 is resin which has the structure of the tricyclo deca nil methacrylate / t-butyl methacrylate / methacrylic acid (50/25/25) which JP,H7-199467,A was alike work-example 2, therefore was prepared. The resin R2 used for the comparative example 2 is the acrylic acid adamanthyl acrylic acid t-butyl (1:1) copolymer prepared according to the work example 3 of JP,H7-234511,A. [0196]

[Table 2]

	樹脂	光酸発生剤	塩基性 化合物	界面 活性剤	溶剤
実施例 1	(1)	PAG4-6=46mg	· 5	W 5	\$1/\$2=7/3
2	(2)	FAG4-39/PAG4-95 =42/8mg	4	W 5	S1/S2=7/3
3	(3)	PAG4-50=45mg	6	W 4	S1/S2=7/3
4	(4)	PAG4-48/PAG4-70 =20/60mg	3	W 3	S1/S2/S3 =70/25/5
5	(5)	PAG4-50/PAG4-67 =40/6mg	2	W 2	S1/S2/S3 =70/25/5
6	(6)	PAG4-52/PAG4-96 =40/5mg	1	W 1	\$1/\$2/\$3 =70/25/\$
7	(7)	PAG4-39=45mg	5	W 5	S4/S2=68/32
8	(8)	PAG4-45=43mg	4/5=1/1	W 5	S5/S6=60/40
9	(9)	PAG4-48=43mg	. 5	W 5	S1/S2=65/35
1 0	(10)	PAG4-52/4-79 =38/20mg	6	W 5	S1/S2=65/35
1 1	(1)	PAG4-3=40mg	なし	なし	S4
1 2	(1)	PAG4-48/PAG4-65 =15/80mg	1	W 5	S1/S2=7/3
1 3	(1')	PAG4-48=42mg	5	W 5	S1/S2=7/3
1 4	(1")	PAG4-52/PAG4-65 =22/70mg	6	W 5	S1/S2=7/3
比較例 1	R.1	PAG6-22=40mg	なし	なし	S1
2	R 2	PAG4-3=40mg	なし	なし	S4

[0197] The sign of each component in Table 2 shows the following.

[Surface active agent]

W1: Mega fuck F176 (made by Dainippon Ink) (fluorine system)

W2: Mega fuck R08 (made by Dainippon Ink)

(Fluorine and silicone system)

W3: Polysiloxane polymer KP-341 (made by Shin-Etsu Chemical Co., Ltd.)

W4: Polyoxyethylene nonyl phenyl ether W5: Troysol S-366 (made in Troy Chemical) [0198] [Amine]

1:1, 5-diazabicyclo [4.3.0]-5-nonene (DBN)

2: Bis(1, 2, 2, 6, and 6-pentamethyl 4-piperidyl) SEBAGETO 3:trioctylamine 4:triphenyl

imidazole 5: express antipyrin 6:2 and 6-diisopropyl aniline. [0199] [Solvent]

S1:propylene-glycol-monomethyl-ether acetate S2: -- propylene glycol monomethyl ether --S3:gamma-butyrolactone S4:cyclohexanone S5:ethyl lactate S6: -- butyl acetate [0200] [Valuation method of the defocusing latitude (DOF) of an isolated line] A spin coater is used for the positive-type-photoresist liquid prepared above. It applied on the silicon wafer, desiccation and about 0.4-micrometer positive-type-photoresist film were produced for 90 seconds at 130 degrees C, and it exposed to it by the ArF excimer laser (the wavelength of 193nm, ArF stepper by an ISI company of NA=0.6). Heat-treatment after exposure is performed for 90 seconds at 120 degrees C, it rinses with development and distilled water in 2.38weight % of a tetramethylammonium hydroxide aqueous solution, and a resist pattern profile is obtained. changing the focus in the case of exposure to -1.0 - +1.0, and observing the obtained isolated line pattern with a scanning electron microscope about a 0.15-micrometer isolated line (a line/space = 1/10), -- a film -- it asked for the range (micrometer) of the focus which remains without carrying out very. This evaluation result is shown in the following table 3. [0201]

[Table 3]

表3	
	孤立パターンの
	デフォーカス
	ラチチュード
	(µm) 0.75
実施例1	I I
2	0.7
3	0.6
4	0.65
5	0.65
6	0.6
7	0.6
8	0.75
9	0.75
1 0	0.75
1 1	0.4
1 2	0.7
1 3	0.75
1 4	0.75
比較例1	0.1
2	0.15

[0202] The result of Table 3 shows that the constituent of this invention is greatly excellent in the defocusing latitude of an isolated pattern.

[0203]

Page 70 of 70

[Effect of the Invention] By this invention, the defocusing latitude of an isolated pattern can
offer the positive resist composition which is greatly excellent.

[Translation done.]